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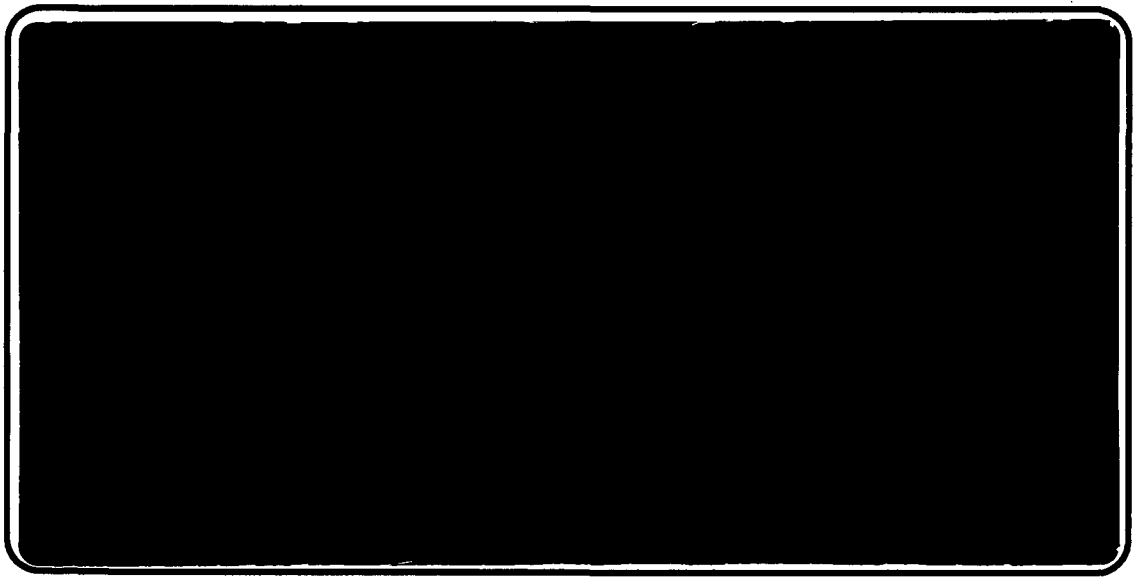

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EXECUTIVE SUMMARY

Determining the solids fraction (or conversely the water fraction) of black liquor can be difficult, particularly for heavy liquors. Isotope dilution analysis is a well-established method of determining water in complex matrices, and the technique was applied to black liquor. The method requires the addition of a small amount of tritiated water to a sample of black liquor, followed by filtration and a determination of the tritium content of the filtrate. This study discusses the assumptions required to apply the procedure to black liquor and demonstrates that a precision of about 1% can be achieved in a 30-minute measurement with quantities of tritium that are exempt from federal regulation.

ABSTRACT

Black liquor solids are determined by tritium isotope dilution analysis. The technique is rapid and sensitive, does not require evaporative separation of water from solids, and is particularly applicable to high levels of solids.

None of the techniques for determining black liquor solids offers the combination of speed, precision, and ruggedness sought after in mill operations (1-3). Gravimetry is precise but time-consuming. Molar refractivity is rapid but is sensitive to temperature changes, and spectroscopic methods suffer from potential interferences. The high solids region is one of particular difficulty.

Isotope dilution analysis (IDA) has been used in several disciplines for determining water (4,5). Essentially, the sample is mixed with tritiated water whereupon the tritium is diluted in proportion to the water present in the sample. The solution is counted, and the water content is determined from the decrease in specific activity. The method is rapid, precise, relatively free from interference, and can be performed with levels of activity

low enough to be exempt from federal licensing requirements. We have explored the feasibility of determining black liquor solids by isotope dilution analysis using levels of activity that are exempt from licensing.

BASIS OF THE METHOD

Consider a situation where V mL of tritiated water (standard) is added to a known mass of black liquor, the mixture is shaken, filtered, and the filtrate counted. If water in black liquor is the only source of exchangeable protons, then

$$[T]_{std}V = [T]_{filtrate}(V + V_{blw}) \quad (1)$$

where $[T]_{std}$ and $[T]_{filtrate}$ are tritium concentrations in the standard and in the filtrate, respectively, and V_{blw} is the volume of water contained in black liquor. Black liquor solids contain hydroxyl and other groups capable of hydrogen isotope exchange, and accounting for these leads to

$$[T]_{std}V = [T]_{filtrate}(V + V_{blw} + 9\alpha f_{exH} m_{solids}) \quad (2)$$

where m_{solids} is the mass of solids in the black liquor, f_{exH} is the weight fraction of exchangeable hydrogens in black liquor solids, α is the tritium/hydrogen fractionation factor, and the multiplier of 9 expresses the mass of exchangeable protons in terms of mL of water. It is assumed that the specific gravity of water is 1. Rearrangement gives

$$f_{solids} = \left[\frac{V}{m_t}\left[\frac{T_{std}}{T_{filtrate}} - 1\right] - 1\right]\frac{1}{(9\alpha f_{exH} - 1)} \quad (3)$$

where f_{solids} is the solids fraction of black liquor, and m_t is the total mass of black liquor used.

RESULTS AND DISCUSSION

A stock black liquor sample was diluted to several compositions, each of which was analyzed for solids by both gravimetry and isotope dilution. Values for f_{solids} determined gravimetrically were regressed against $(V/m_t)(T_{std}/T_{filtrate} - 1)$ in eq. 3 to give a slope and intercept of -0.96 (σ=0.11) and 1.19 (σ= 0.007), respectively. Values of f_{solids} calculated with these parameters are listed in the "IDA" column of Table 1. Replicate analysis of

analysis of the 67% black liquor sample gave a standard deviation of 1.2% (n=7). Since counting precision is better at higher levels of activity, the overall precision should be best at high f_{solids}, in contrast to other methods of determination.

These uncertainties are preliminary and should be interpreted in light of the conditions used. First, since the black liquors derived from a single stock, αf_{exH} was constant. This term will vary somewhat with changes in the organics/inorganics ratio and other factors. The variablility is likely to be small since the total hydrogen content of black liquor solids is low, and the exchangeable fraction must, therefore, be even lower. The counting uncertainty of 0.5% was a major component of the overall uncertainty. This can easily be reduced through use of higher levels of activity. The most significant source of uncertainty was probably the manipulation of microliter quantities of solution.

A major advantage of isotope dilution over gravimetry is speed. An analysis can be completed in about 30 minutes or faster if higher activities are used. The isotopic method lends itself well to automation. The single weighing, filtering and counting sequence is well within the capability of an inexpensive robotics system, use of which should also improve precision. On balance, if speed is not an issue, gravimetry is the preferred technique. If turnaround is important, then the precision and stability of the isotope dilution technique positions it favorably among other methods, particularly for samples rich in solids.

A value for αf_{exH} can be extracted from either the slope or the intercept listed above. The uncertainty in slope is higher than that in intercept, probably because it is more directly affected by variations in m_t. Since gravimetrically determined f_{solids} were used in eq. 3, we are effectively assuming that water is the only species lost upon heating; i.e., no account is taken of organic volatiles or of thermal degradation. The intercept is less sensitive to these effects and corresponds to a αf_{exH} value of 0.018. The fractionation factor, α, is not known. If a value of one is tentatively assigned, then exchangeable protons (which are probably mainly associated with the hydroxyl group) constitute 1.8% of the solids, or 47% of the total hydrogen content.

CONCLUSIONS

Our exploratory study establishes the feasibility of using isotope dilution analysis for determining black liquor solids. The precision of the method is about 1% at 67% solids, and sample processing requires about 30 minutes. The amount of activity

necessary is several orders of magnitude below the level at which a license would be required. Precision is best for heavy liquors.

EXPERIMENTAL PROCEDURES

A sample of black liquor was obtained from the Weyerhaeuser Mill in New Bern, NC. Elemental analysis of the solids gave: Na (18.2%), K (1.1%), C (37.0%), H (3.8%), O(33.3%), S(4.6%), and Cl (0.7%). The black liquor was diluted with water to different compositions, each of which was analyzed for solids by both gravimetry and isotope dilution.

In a typical IDA experiment, a vial containing about 1 g. of black liquor was mixed vigorously (in a vortex mixer) with 1 mL of water containing ^3H_2O. The tritium in the sample corresponded to 118 nCi. The mixture was filtered through a 0.45 μ PTFE membrane filter, and 5 μL of the filtrate were added to a scintillation vial containing Beckman Ready Solv HP and 100 μL of acetic acid (to suppress chemiluminescence), and counted. Five microliters of the stock tritiated water were then added to the vial as an internal standard, and a recount was taken. Counting precision was about 0.5%. A control (without black liquor) processed through the filtration-counting sequence gave a recovery of 99.5%. The data in Table 1 are corrected for an average background of 21 cpm.

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